# Syntheses of Novel Fullerene Tweezers and Their Supramolecular Inclusion Complex of $C_{60}$

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Fullerene tweezers which have a rigid acetylenic spacers were synthesized and their inclusion abilities for $C_{60}$ were examined by UV spectroscopy. From the spectra, the association constants were determined using Benesi-Hildebrand method. Fullerene tweezers with a 1,4-bis(4-oxycarbonylphenyl)butadiyne spacer showed the highest association constant for $C_{60}$ (39300±250 dm$^3$mol$^{-1}$ in benzene).

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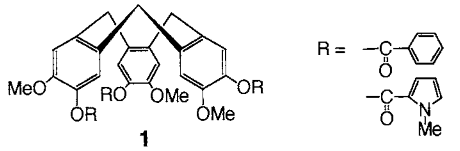
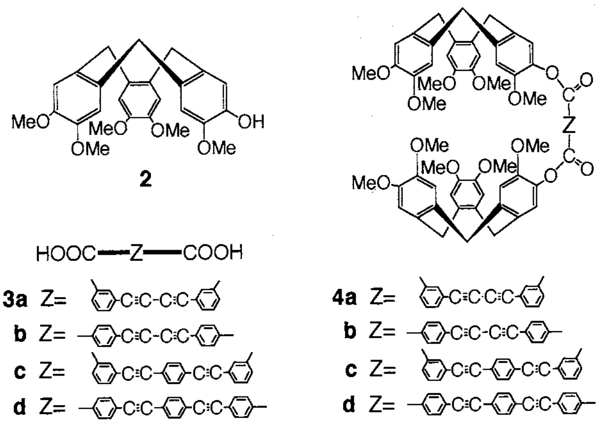
The recent publication[1] of supramolecular complexes between fullerenes and the unique host molecules incorporating two calix[5]arene prompted us to investigate the design at another type of fullerene tweezers having two cyclotriveratrylene (CTV) units as the receptive center. The attractive properties of CTV derivatives **1**[2] with aromatic pendants characterized by the presence of an efficient inclusion ability toward $C_{60}$ fullerene, directed our continuing efforts to the synthesis of fullerene tweezers **4** with two CTV units at the both ends of acetylenic spacer which should display efficient supramoleclar complex with $C_{60}$.



**1**

Starting from ethyl *m*- or *p*- bromobenzoate, various acetylenic spacers **3** were synthesized as shown below. Oxidative coupling of ethyl *m*-ethynylbenzoate with copper(II) acetate[3] followed by hydrolysis gave the diacid **3a** and cross-coupling reaction between two equivalent ethyl *m*-ethynylbenzoate and *p*-dibromobenzene in the presence of palladium catalyst[4] followed by hydrolysis provided the diacid **3c**. The other acid spacer **3b** and **3d** were also prepared in the same way from ethyl *p*-ethynylbenzoate. Finally, esterification between the diacid **3** with two equivalent of CTV-OH **2**[5] by using DCC and DMAP,[6] afford the fullerene tweezers **4a**[7] (33%), **4b**[8] (53%), **4c**[9] (75%), and **4d**[10] (19%), respectively.



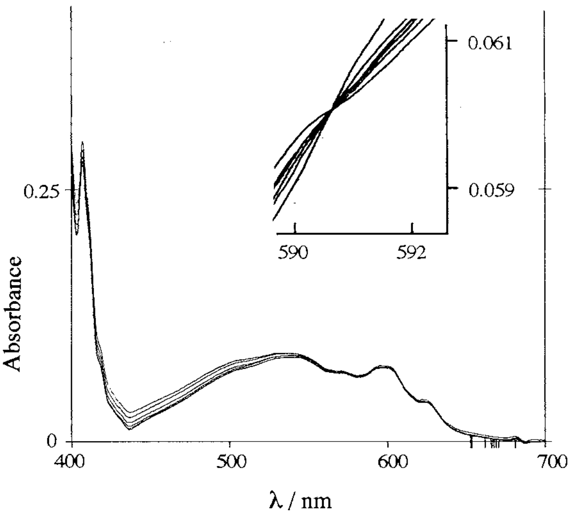


**Figure 1.** Absorption spectra of $C_{60}$ ($1.09 \times 10^{-4}$ mol dm$^{-3}$) in the presence of fullerene tweezers **4c** in benzene. The concentration of **4c** are from the bottom: 0.0, 0.11, 1.10, 5.48, 11.20, 16.05 ($\times 10^{-3}$ mol dm$^{-3}$). Temperature : 298 K.

Immediate color change from purple to yellow was observed on mixing $C_{60}$ and the fullerene tweezers solution. This is ascribed to the formation of host-guest complex in solution.

Job's plot[11] and isosbestic points at 591 nm (Figure 1) between $C_{60}$ and host fullerene tweezers **4a**, **4b**, and **4c**, provided evidence for a 1:1 complex in solution. The association constant of the complexes determined from the differences of absorbance at 430-440 nm region using Benesi-Hildebrand (B-H) method.[12]

Table 1 lists the association constant obtained by titration of **4** to $C_{60}$ at 298 K (λ 430-440 nm).[13] Table 1 shows association constants are dependent on the solvent and length of the acetylenic spacers in the host, and **4b** (39300±250 dm$^3$mol$^{-1}$ in benzene) has the highest association constant than **4a**, **4c**, and

**Table 1.** Association constants (dm$^3$mol$^{-1}$) for $C_{60}$ at 298 K[a]

| | benzene | toluene | *o*-dichlorobenzene |
|---|---|---|---|
| **4a** | 18100±110 | 6300±50 | 6300±40 |
| **4b** | 39500±250 | 23600±100 | 5800±50 |
| **4c** | 14000±170 | 23000±390 | 13200±150 |
| **4d** | < 300 | < 300 | < 300 |

[a] λ=430-440 nm.

**4d** toward $C_{60}$. $^{13}$C NMR spectra of $C_{60}$ were measured in the presence of **4**. The largest complexation-indeced upfield shift $\Delta\delta$ (0.30) of $C_{60}$ was observed, when the equimolar amount of $C_{60}$ and host **4b** were present in $C_6D_6$. These observations are compatible with examination of Corey-Pauling-Kolton (CPK) space-filling molecular models of **4** which reveal that the host cavity of **4b** (*ca.* 13 Å innner diameter) composed of two CTV units is especially well suited cavity size for complexation of $C_{60}$.

The association constant for $C_{70}$ was also determined by the same method. Only host **4c** showed inclusion ability for $C_{70}$ in solution (2700±50 dm$^3$mol$^{-1}$ in benzene, 1600±50 dm$^3$mol$^{-1}$ in toluene).

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7 **4a**: white powder, mp 152-154 ℃, IR (KBr): 2100 ($C\equiv C$), 1700 (C=O), 1510(Ar), 1260 cm$^{-1}$ (C-O), $^1$H NMR ($CDCl_3$): $\delta$ 3.60 (m, 6H, $CH_2$), 3.83 (m, 30H, $CH_3$), 4.82 (t, J=14.4 Hz, 6H, $CH_2$), 6.79 (s, 2H, ArH of CTV unit), 6.83 (s, 2H, ArH of CTV unit), 6.85 (s, 2H, ArH of CTV unit), 6.86 (s, 2H, ArH of CTV unit), 6.98 (s, 2H, ArH of CTV unit), 7.13 (s, 2H, ArH of CTV unit), 7.39 (t, J=7.6 Hz, 2H, ArH of the spacer), 7.77 (d, J=7.6 Hz, 2H, ArH of the spacer), 8.18 (dd, J=7.6, 2.6 Hz, 2H, ArH of the spacer), 8.35 (d, J=2.6 Hz, 2H, ArH of the spacer), MS (FAB) m/z 1126 (M$^+$).

8 **4b**: white powder, mp >300 ℃, IR (KBr) 2100 ($C\equiv C$), 1700 (C=O), 1505 (Ar), and 1260 cm$^{-1}$ (C-O), $^1$H NMR ($CDCl_3$): $\delta$ 3.59 (m, 6H, $CH_2$), 3.82 (m, 30H, $CH_3$), 4.82 (m, 6H,$CH_2$), 6.84 (m, 6H, ArH of the CTV unit), 6.98 (s, 2H, ArH of the CTV unit), 7.12 (s, 2H, ArH of CTV unit), 7.64 (d, J=8.6 Hz, 4H, ArH of the spacer), 8.16 (d, J=8.6 Hz, 4H, ArH of the spacer), MS (FAB) m/z 1126 (M$^+$).

9 **4c**: white powder, mp 162-168 ℃, IR (KBr): 2100 ($C\equiv C$), 1710 (C=O), 1500 (Ar), 1250 cm$^{-1}$ (C-O), $^1$H-NMR ($CDCl_3$): $\delta$ 3.62 (m, 6H,$CH_2$), 3.83 (m, 30H, $CH_3$), 4.82 (t, J=14.5 Hz, 6H, $CH_2$), 6.83 (m, 8H, ArH of CTV unit), 6.99 (s, 2H, ArH of CTV unit), 7.13 (s, 2H, ArH of CTV unit), 7.50 (t, J=7.6 Hz, 2H, ArH of the spacer), 7.53 (s, 4H, ArH of the spacer), 7.77 (d, J=7.6 Hz, 2H, ArH of the spacer), 8.16 (2H, d, J=7.6 Hz, Ar), 8.35 (s, 2H, ArH of the spacer), MS (FAB) m/z 1203 ([M+H]$^+$).

10 **4d**: white powder, mp 240-242 ℃, IR (KBr): 2100 ($C\equiv C$), 1700 (C=O), 1500 (Ar), 1260 cm$^{-1}$ (C-O), $^1$H NMR: $\delta$ 3.62 (m, 6H,$CH_2$), 3.83 (m, 30H,$CH_3$), 4.82 (t, J=14.7 Hz, 6H,$CH_2$), 6.83 (m, 8H, ArH of CTV unit), 6.98 (s, 2H, ArH of CTV unit), 7.14 (s, 2H, ArH of CTV unit), 7.56 (s, 4H, ArH of the spacer), 7.65 (d, J=8.3 Hz, 4H, ArH of the spacer),8.18 (d, J=8.3 Hz, 4H, ArH of the spacer), MS (FAB) m/z 1203 ([M+H]$^+$).

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13 We also determined the association constant using improved Benesi-Hildebrand method reported by Rose et al. (N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, **81**, 6138 (1959)), however, there were practically no difference between both of the data.